

EXC-TR-95-015

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**Technical Report
1021**

**A Strategy for Higher Temperature
Superconductivity in the Layered Cuprates**

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10 July 1995

Lincoln Laboratory

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

LEXINGTON, MASSACHUSETTS



Prepared for the Department of the Air Force under Contract F19628-95-C-0002.

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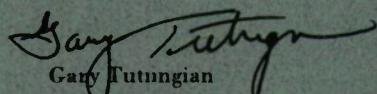
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**A STRATEGY FOR HIGHER TEMPERATURE
SUPERCONDUCTIVITY IN THE LAYERED CUPRATES**

G.F. DIONNE
Group 63

TECHNICAL REPORT 1021

10 JULY 1995

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ABSTRACT

Recent attempts to raise the critical temperatures of cuprate superconductors are reviewed and discussed in terms of covalent electron transfer between Cu ions of mixed valence. A report of possible superconductivity effects at 250 K is examined from the standpoint of ABO_2 parent-cell building blocks identified as superconducting by Goodenough and his students at the University of Texas. Based on the mounting evidence that cation mixed valence is responsible for the superconductivity in these compounds, compositions $(Ca_{1-x}Na_x)CuO_2$, $(Sr_{1-x}Ag_x)CuO_2$, and $(Ba_{1-x}K_x)CuO_2$ are proposed as chemical systems for obtaining superconductors with maximum feasible critical temperatures.

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1. INTRODUCTION

Reported superconductivity behavior at temperatures above 200 K [1] has rekindled hopes that room temperature superconductors may be possible. The purpose of this study is to examine some of the recent activity in the context of theoretical concepts and analyses published earlier [2,3] and to propose materials engineering objectives for achieving the highest critical temperatures T_c with the cuprate systems currently under study. The use of sequentially imposed layer epitaxy (SILE), an advanced version of molecular beam epitaxy, represents the type of approach recommended in Dionne [2, p. 62] to achieve the spatial ordering of carriers required to maximize T_c .

2. CONDITIONS FOR SUPERCONDUCTIVITY

A basic idea of the covalent electron transfer (CET) model [3] is that a homogeneous density of supercarriers (the $\nabla n_s = 0$ condition imposed by the London theory) may be achieved by a dynamic ferroelectric transition in which mobile carriers are linked to fixed charges (large polaron arrays). Foremost among the many conditions required for superconductivity, therefore, would be coherent transfer of carriers between polaron “cells.” A basic recommendation given in Dionne [2] for increasing the critical temperature and current density is to raise the polaron density by introducing ions of different valence or by creating lattice vacancies (charge removal), and then to control the dispersal (metastable, if necessary) of the charge sources by means of SILE-type processing techniques.

In the cuprate systems where superconductivity has been observed, certain structural and chemical features are common among all of them:

- Perovskite-type cell structure with 180-deg Cu-O-Cu bonds to link Cu $d_{x^2-y^2}$ orbitals covalently with $2p$ orbitals of O²⁻ ions;
- Opportunity for different valence states (1+, 2+, and 3+) of Cu ions induced by mixtures of metal ions of fixed charges or a combination of lattice deficiencies, i.e., empty sites;
- Cu ions surrounded by oxygen complexes of tetragonal/orthorhombic crystal-field symmetry caused by *c*-axis elongated octahedra (Cu-O₆), pyramids (Cu-O₅), or planes (Cu-O₄) in the higher T_c compositions.

As discussed in Appendix D of Dionne [3], the axial crystal fields produced by these oxygen coordinations split the $d_{x^2-y^2}$ state from the lower d_{z^2} or d_{xy} state to provide enhanced stabilizations of the hopping carriers, i.e., increased activation energy E_{hop} , as diagramed in Figure 1. Moreover, activation energies should be expected to increase with cation valence, meaning that zero-spin Cu³⁺ “holes” should be more stable than Cu¹⁺ “electrons.” To some extent this reasoning is supported by experiment, where *p*-type superconductors with Cu²⁺⁽³⁺⁾ transfers have been found to have generally higher T_c values than corresponding *n*-type Cu¹⁺⁽²⁺⁾ transfers in similar coordinations.

For the three coordinations available, a revision of earlier work [3] that takes into account decreases in exchange integral energy with increasing polaron density has led to the conclusion that approximate E_{hop} values are likely to be 4 meV (32 cm⁻¹) for Cu-O₆, 10 meV (~ 80 cm⁻¹) for Cu-O₅, and 12 meV (~125 cm⁻¹) for Cu-O₄ planes. A proposed theoretical model of the variation of T_c with polaron carrier concentration is presented in Figure 2 for the different superconductor classes of interest.

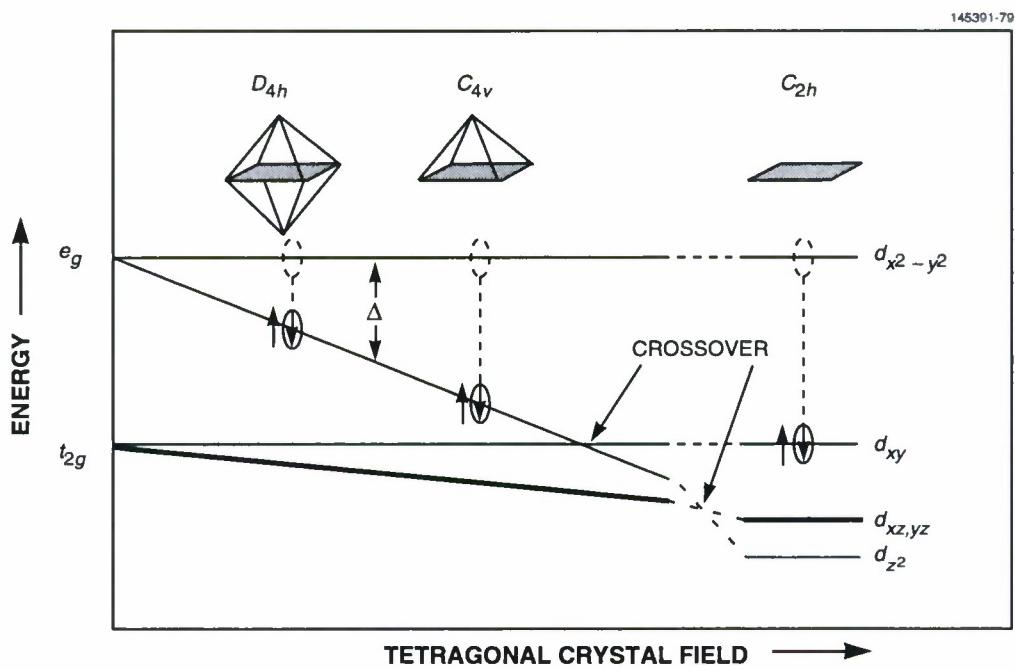


Figure 1. Growth of the $\text{Cu}^{3+} \text{d}^8$ low-spin state ($S = 0$) stabilization by e_g doublet splitting Δ as the tetragonal crystal-field component progresses through distorted octahedron (D_{4h}) \rightarrow pyramid (C_{4v}) \rightarrow plane (C_{2h}).

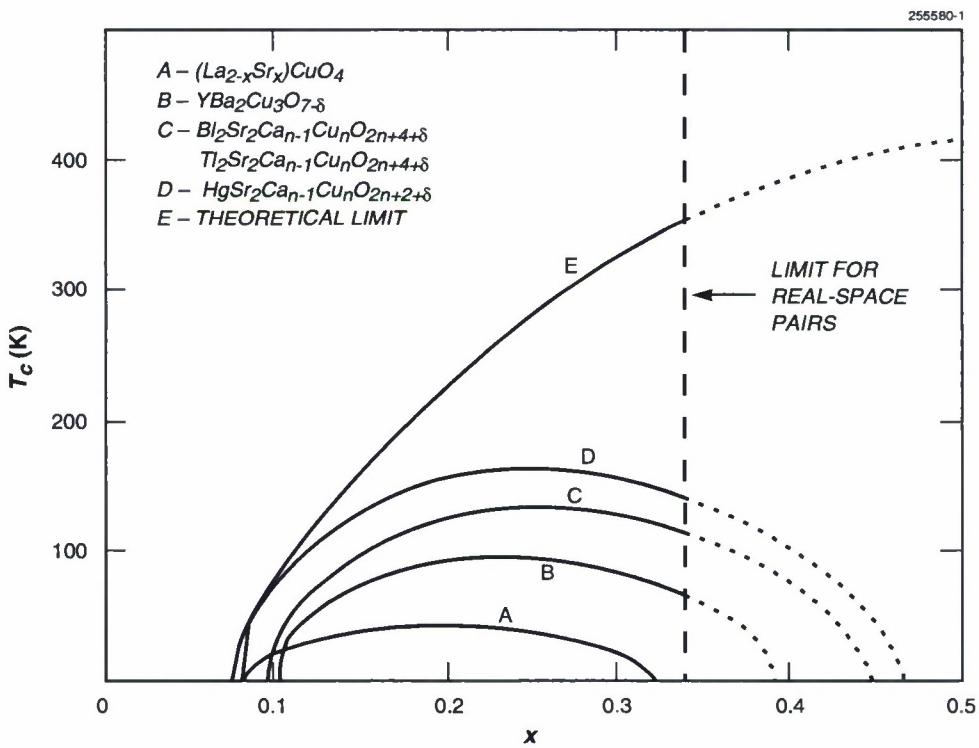


Figure 2. CET theory projection of critical temperatures for cuprate superconductors as functions of polaron charge density. The parameter δ denotes the O^{2-} vacancy concentration, which may be expressed in terms of x . Other parameters not listed are the activation energy for electron hopping and the degree of polaron dispersal. Curve D illustrates the enhancement of T_c caused by increased covalent exchange integrals when prepared under high pressure. Curve E is a proposed limit for perfect polaron source dispersal.

3. CHEMISTRY AND CRYSTALLOGRAPHY

Consider the case of a perovskite cubic cell of Figure 3(a) for the generic formula $A^{3+}B^{3+}O_3^{2-}$. Based on electrostatic arguments, this compound should not accept Cu ions in the 2+ state. Note also that the B site, which is assigned to the Cu ions, is not a host for superconductivity because the O_6^{2-} coordination forms a perfect octahedron. The building block of the artificial layered superconductors is actually carved out of this basic cell by removing the O_6^{2-} ions from the upper and lower planes, thereby creating the desired

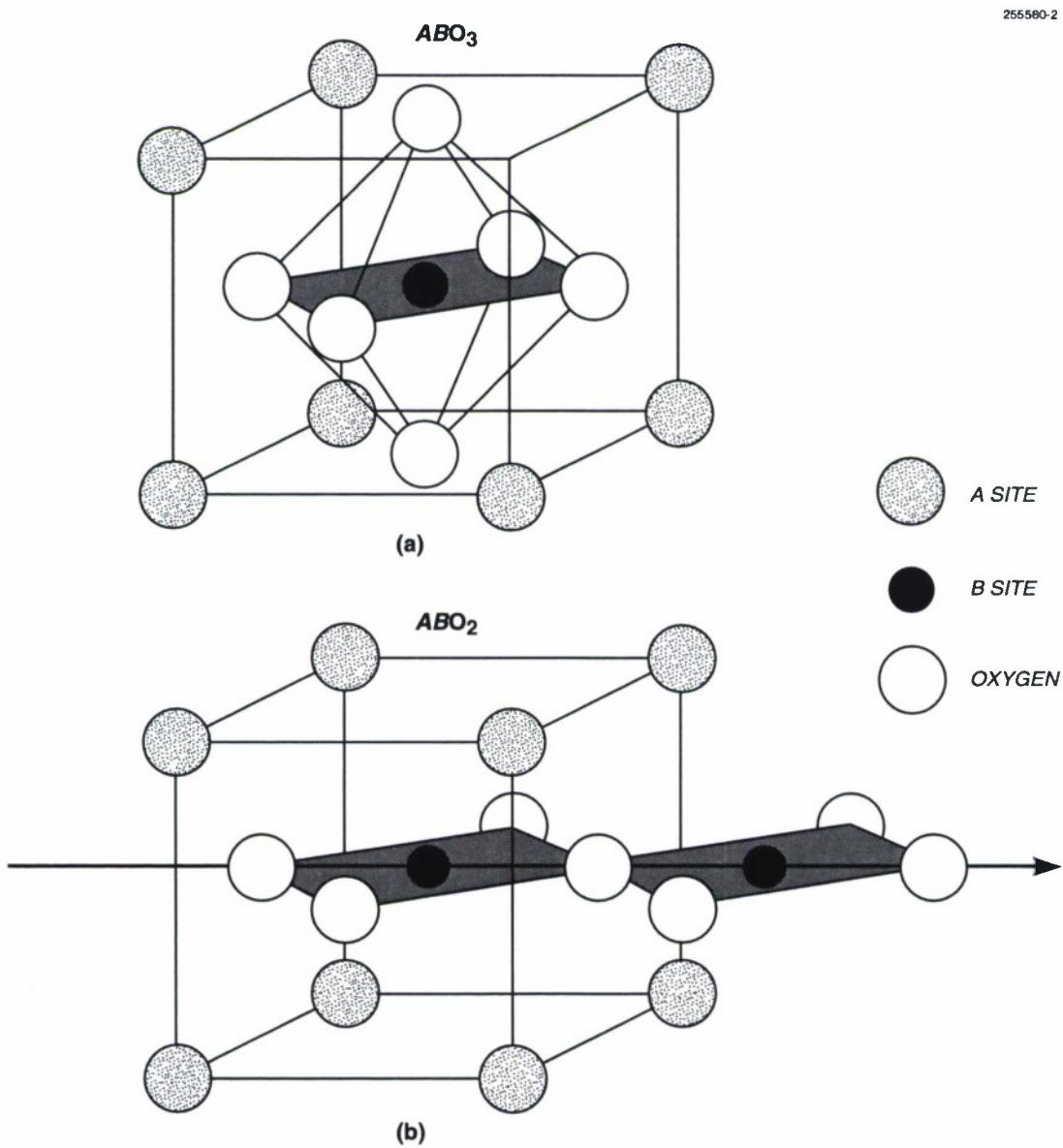


Figure 3. Perovskite structures: (a) basic cubic cell with octahedrally (O_6) coordinated B site, and (b) primitive tetragonal cell with square planar (O_4) coordinated B site.

Cu-O_4 planar arrays. If Figure 3(a) is redrawn accordingly, one can see how the $\text{Cu}^{2+}\text{O}_2^-$ layers are formed with the “naked” layers of A^{2+} ions acting both to restore charge neutrality and to isolate the CuO_2 layers. Since this operation amounts to the removal of one-third of the O^{2-} ions, the chemical formula must now read $A^{2+}\text{B}^{2+}\text{O}_2^-$. In the multilayered compounds, Ca^{2+} and Sr^{2+} ion combinations are used for the A^{2+} layers of Figure 3(b). This “parent structure” was synthesized by Siegrist et al. [4] with a fully stoichiometric $(\text{Ca}^{2+})_{0.86}\text{(Sr}^{2+})_{0.14}\text{CuO}_2$. As would be expected, the composition was an insulator.

The configuration of Figure 3(b) fulfills only part of the preceding requirements. As proposed previously in detail [2,3] and later concluded by Raveau [5] and Smith et al. [6], for electrical conduction to occur in the CuO_2 layer, the Cu ions must assume mixed valence states. There are various ways to establish Cu^{3+} or Cu^{1+} populations in metal oxides. Substituting 1+ or 3+ ions into the A^{2+} layer will tend to force Cu into the offsetting 3+ and 1+ states, thereby creating *p*- or *n*-type conductivity, respectively, through electron exchange with host Cu^{2+} ions. Depleting the A^{2+} layer will also induce Cu^{3+} ions but at the risk of causing structural defects from the combined local distortion effects of the vacancies. Restoring some of the O^{2-} ions by oxidation will also create Cu^{3+} , but that will disrupt the array of Cu-O_4 planar complexes mentioned earlier as a condition that is favorable for superconductivity. Another approach is to introduce mixed valence or defect populations in a La, Tl, Bi, or Hg oxide layer (not shown in Figure 3) that can be remote from the $A^{2+}\text{Cu}^{2+}\text{O}_2^-$ cells. These “charge reservoir” blocks, as described in Laguës et al. [1], are apparently used to establish the mixed valence condition in the adjacent CuO_2 planes.

4. MULTIPLE VERSUS SINGLE BLOCKS

The concept of stacking multiple $\text{Ca}^{2+}\text{Cu}^{2+}\text{O}_2^-$ blocks sandwiched between nonsuperconducting layers containing a variety of large cations is being promoted as the approach for maximizing T_c [1]. There is no obvious rationale for this belief based on charge transfer considerations alone. Covalent transfer in the direction normal to the CuO_2 planes cannot take place in any substantial way because the lobes of the electron-occupied $d_{x^2-y^2}$ antibonding orbitals (or bands, if you prefer) of the occupied Cu ions do not extend in that direction. This anisotropic geometric condition also accounts for the small coherence lengths along the c axis, as well as the anisotropy of the physical properties of the cuprate superconductors in general. Only in certain noncuprate superconducting perovskites, such as $(\text{K}^{1+})_{1-x} \text{Ba}^{2+}_x (\text{Bi}^{5+}_{1-x} \text{Bi}^{4+}_x) \text{O}_3$, where isotropic 6s orbital states of Bi^{4+} would be involved, can the orbital overlaps in the z (or c -axis) directions have a direct influence. In the $[\text{Bi}^{3+}_r \text{Sr}^{2+}_2 \text{O}_4 \cdot \text{Cu}^{2+} \text{O}_2]_{3r-6} (\text{Ca}^{2+}\text{Cu}^{2+}\text{O}_2)_{n-1}$ system depicted in Figure 4 for $n = 4$, the $r < 2$ condition would cause negative charges to appear in the charge reservoir block attached to a CuO_2 layer, provided that the Cu ions remain in the 2+ state. To compensate for this charge imbalance, either some of the Cu will become 3+ to produce mobile “holes” or more likely, the Bi will increase its valence from 3+ to 4+ or 5+ to produce hole conduction of its own within the reservoir blocks themselves. If Cu is affected, then both Cu^{3+} and Cu^{1+} will probably occur in the layers attached to the charge reservoir blocks.

It should be pointed out that when Tl^{3+} or Hg^{2+} is used instead of Bi in these layers, the opportunity for charge compensation within the charge reservoir is less likely, because unlike Bi^{3+} , these elements do not accept higher valence states. Since the charge compensation would have to take place through Cu^{3+} formation, this may also explain why the Tl and Hg compounds have generally shown T_c values higher than those of the Bi compositions.

If the mixed valence in the charge reservoirs serves only to disrupt the polaron formation where it is needed for superconductivity, one is led to speculate that the source of higher T_c values may simply be related to structural advantages that are realized with the creation of the multiple $(\text{Ca}^{2+}\text{Cu}^{2+}\text{O}_2)_{n-1}$ blocks that contain cells that are progressively farther away from the disordered charge reservoirs, as illustrated in Figure 5. Since the depletion of Bi is accomplished by annealing in a reducing atmosphere, it is likely that Ca^{2+} is also lost in this process [7], thereby providing the source of polarons within the CaCuO_2 blocks. Because the Ca^{2+} vacancies would represent 2- charges at the empty lattice sites, they would act as polaron charge sources, and their dispersal would be encouraged by repulsion fields that act to minimize the Madelung energy.

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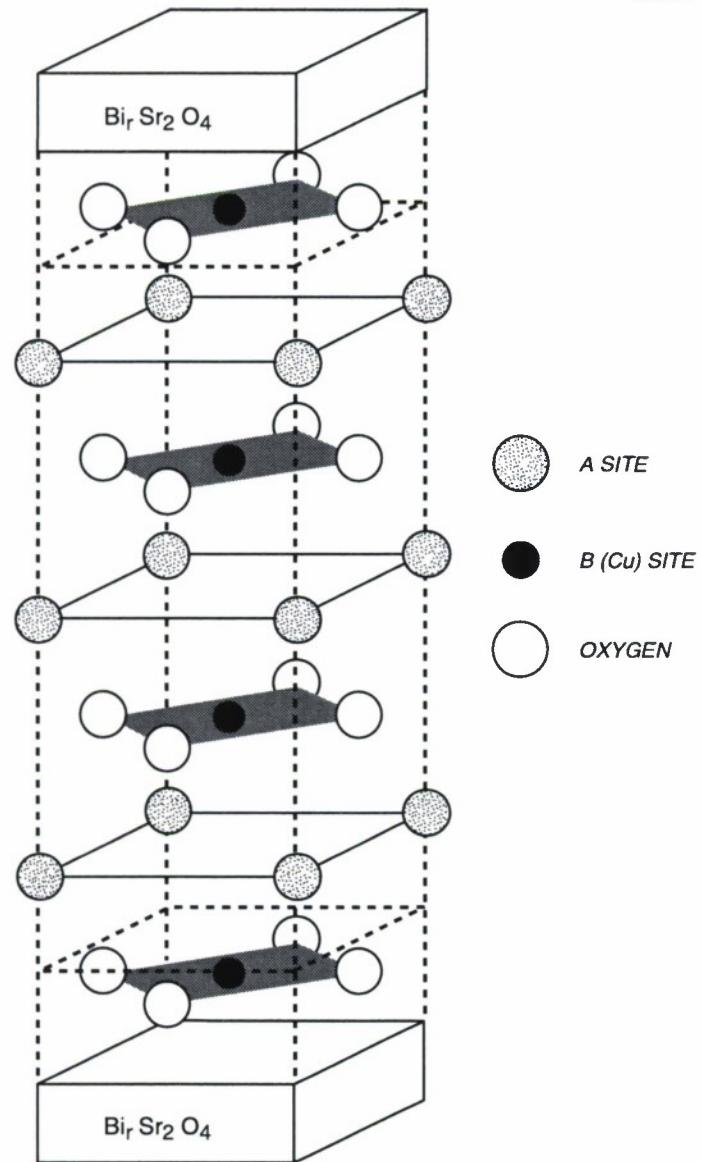


Figure 4. Layered concept for superconductivity with multiple ABO_2 "blocks" stacked vertically and sandwiched between "charge reservoir" blocks (Bi, Tl), Sr_2O_4 that act as "book ends."

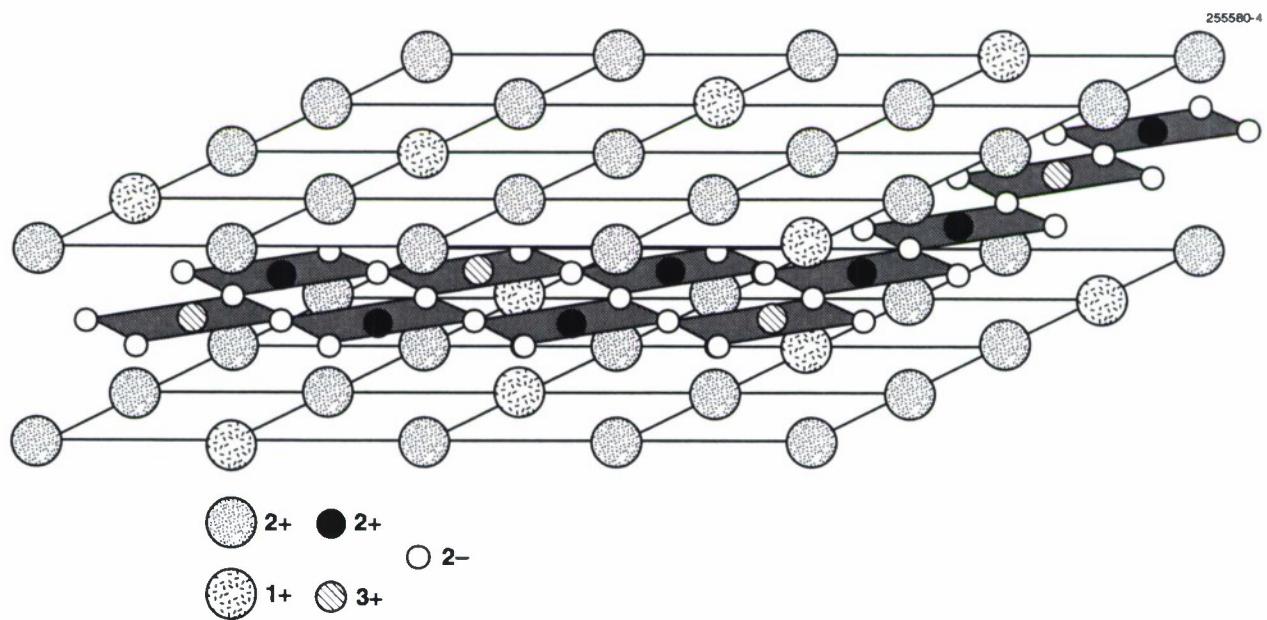


Figure 5. Model of charge dispersal in “naked” compound of primitive ABO_2 cells. Charges that act as polaron sources are induced by a mixture of ionic valences in the A-site layers.

5. APPROACH FOR INCREASING T_c

In previous discussions of the role of cation valence states in determining the density of *p*-type polarons in $\text{YBa}_2\text{Cu}_3\text{O}_7$ [2,3], it was concluded that Cu^{3+} ions in the CuO_2 planes occurred as a result of O^{2-} anion vacancies. The Cu^{3+} density could be increased further by substituting lower valence alkali metal cations such as Na^{1+} and K^{1+} or noble metals Ag^{1+} and Au^{1+} for Y^{3+} or Ba^{2+} , whichever is more compatible crystallographically based on ionic radii and site size considerations. For the composition $\text{Y}^{3+}\text{Ba}^{2+}_{2-x}\text{Ag}^{1+}_x[\text{Cu}^{2+}_{0.75-x/2}\text{Cu}^{3+}_{0.25+x/2}]_2[\text{Cu}^{2+}_{0.5}\text{Cu}^{3+}_{0.5}]\text{O}_7$ [3, p. 91], an increase in Cu^{3+} concentration in the CuO_2 layers (here the basal planes of pyramidal oxygen coordinations) could raise the critical temperature, provided that the cation dispersal is also improved.

This general approach to raising the density of carriers by introducing ionic charge imbalances can be applied to any of the layered cuprates. If the parent cells can exist without the reservoir blocks, and if carriers can be induced in the CuO_2 layers by creating fixed charges in the A^{2+} layers in the form of 2- vacancies, a strategy for exploiting the tendency for vacancies to disperse would be to impose vacancies during deposition of the Ca^{2+} layers by truncating the layer formation prior to its completion. Alternatively, 1+ ions could be mixed with Ca^{2+} to allow the formation of complete layers. As depicted in Figure 5, Na^{1+} should disperse more easily than vacancies because Na^{1+} has a radius (0.95 Å) similar to that of Ca^{2+} ions (0.99 Å), and any defects that would be caused by vacancies would then be minimized. An alternative combination would be Ag^{1+} substituted into a Sr^{2+} layer. Although the ionic radius of Ag^{1+} is larger (1.26 Å), it is reasonably close to that of Sr^{2+} (1.13 Å) so that clustering tendencies from elastic distortions may be negligible. It also has a lower volatility and higher sticking coefficient. A third possibility could be K^{1+} (1.33 Å) substituted into a Ba^{2+} (1.35 Å) layer, provided that ions of this size could be accommodated into the primitive parent cell. There are at least two examples of superconductivity in the parent $AB\text{O}_2$ compounds. By substituting a 3+ ion in the A^{2+} layer, Cu^{1+} ions are induced. In the cases reported, Smith et al. [6] used Sr^{2+} as A^{2+} in $(\text{Sr}^{2+}_{1-x}\text{Nd}^{3+}_x)(\text{Cu}^{2+}_{1-x}\text{Cu}^{1+}_x)\text{O}_2$ and Miyamoto et al. [8] followed the same strategy for $(\text{Sr}^{2+}_{1-x}\text{La}^{3+}_x)(\text{Cu}^{2+}_{1-x}\text{Cu}^{1+}_x)\text{O}_2$. In both cases, the conductivity was judged to be *n*-type, which is characteristic of Cu^{1+} formation. Critical temperatures, however, were only about 40 K, possibly due to increased lattice parameters in the CuO_2 planes caused by the larger Cu^{1+} ions that could lower covalent transfer probabilities or reduce polaron trapping energies [3].

There was also a report of a *p*-type superconductor that was formed by depletion of ions from the A^{2+} layer [9], here a mixture of Sr^{2+} and Ca^{2+} ions, $(\text{Sr}^{2+}_{1-x}\text{Ca}^{2+}_x)_{1-y}(\text{Cu}^{2+}_{1-2y}\text{Cu}^{3+}_{2y})\text{O}_2$, with $y \approx 0.1$. In this compound, Cu^{3+} occurred with a reduced lattice parameter and a correspondingly higher $T_c = 110$ K. For this work, two other comments are appropriate: first, the A^{2+} layer vacancies appear to have been inhomogeneously distributed and also to have caused structural defects in those layers, and second, the value of $y \approx 0.1$ is therefore only the average value of a range that could have been $0 \leq y \leq 0.2$. A similar situation was reported by Norton et al. [10] with only Sr^{2+} in the partially depleted A^{2+} layer, $\text{Sr}^{2+}_{1-x}(\text{Cu}^{2+}_{1-2x}\text{Cu}^{3+}_{2x})\text{O}_{2-\delta}$, for which a resistive transition suggestive of superconductivity was observed at 185 K. In this case, O_2 deficiencies were also present, and since they could occur only in the CuO_2 planes, superconductivity was probably precluded. Moreover, the absence of O^{2-} ions would have created Cu^{1+} ions that would account for the *n*-type conduction observed, not unlike that which occurs in the Cu(I) planes of $\text{YBa}_2\text{Cu}_3\text{O}_7$ [2,3].

Guidelines for obtaining higher T_c values are the following:

- The *p*-type conductors created by $\text{Cu}^{2+}(3+)$ combinations provide higher T_c in general.
- The occurrence of $\text{Cu}-\text{O}_4$ coordinations with the largest axial crystal-field splitting of the d_{z^2} and $d_{x^2-y^2}$ orbital states must be maximized, which is achieved through the creation of isolated CuO_2 planes.
- To obtain Cu^{3+} , either A^{2+} vacancies or monovalent cations such as noble metals Ag^{1+} , Au^{1+} or volatile alkali metals Na^{1+} , K^{1+} substituted into the A^{2+} layer may be considered. Although more efficient because each vacancy would produce two Cu^{3+} ions, the former option could introduce structural problems if the vacancy density is too high and too inhomogeneous.
- To maximize T_c , an ordered dispersal of charge sources, i.e., $1+$ ions or vacancies, should be established within the A^{2+} planes without clustering.
- To prevent O^{2-} vacancies from occurring in the CuO_2 planes where superconductivity takes place, materials should be prepared in an atmosphere of high O_2 pressure.

6. CONCLUSIONS

Table 1 lists various high- T_c systems of interest in the approximate chronological sequence of their discovery. Note that the reported T_c values follow the general trends mentioned earlier in this report: higher T_c values are likely to be found with *p*-type compounds of lower oxygen coordination surrounding the Cu site. Only the family containing Hg seems to oppose this trend, but that could be the result of Hg enhancing the covalent interaction between the Cu ions. The simplest compounds that fulfill the requirements for highest T_c without cation vacancies would comprise the primitive cell structure, $(\text{Ca}^{2+})_{1-x}(\text{A}^{1+})_x(\text{Cu}^{2+})_{1-x}(\text{Cu}^{3+})_x\text{O}^{2-}_2$. This compound is based on that prepared by Azuma et al. [9] but with A^{1+} replacing the A^{2+} -layer vacancies. Synthesis of this material would probably require SILE or some related process because of the volatility of all three cations. If ordering of A^{1+} in the A^{2+} layers can be achieved, optimum T_c values may be obtainable. Compounds with cations suitable for this procedure based on ionic size matching (listed in Table 2) to promote dispersal and reduce lattice defects are $(\text{Ca}^{2+})_{1-x}(\text{Na}^{1+})_x(\text{Cu}^{2+})_{1-x}(\text{Cu}^{3+})_x\text{O}^{2-}_2$, $(\text{Sr}^{2+})_{1-x}(\text{Ag}^{1+})_x(\text{Cu}^{2+})_{1-x}(\text{Cu}^{3+})_x\text{O}^{2-}_2$, and possibly $(\text{Ba}^{2+})_{1-x}(\text{K}^{1+})_x(\text{Cu}^{2+})_{1-x}(\text{Cu}^{3+})_x\text{O}^{2-}_2$. As indicated in Figure 2, an A^{1+} concentration greater than 25% ($x > 0.25$) in the A layer with high dispersal ($\beta \rightarrow 0$) would be the objective.

TABLE 1
Summary of High- T_c Superconductors

Composition	Polaron Source	Carrier Ion -(n), +(p)	T_c (max) K	Coordination
Reported				
(La _{2-x} Sr _x)CuO ₄	[Sr ²⁺] ⁻	[Cu ³⁺] ⁺	40	Tetragonal Cu-O ₆
(La _{2-x} Ce _x)CuO ₄	[Ce ⁴⁺] ⁺	[Cu ¹⁺] ⁻	24	Tetragonal Cu-O ₆
YBa ₂ Cu ₃ O ₇	O ²⁻	[2Cu ³⁺] ²⁺	95	Pyramidal Cu-O ₅
Bi ₂ Sr ₂ Ca _{n-1} Cu _n O _{2n+4+δ}	O ²⁻	[2Cu ³⁺] ²⁺	120	Planar Cu-O ₄
Tl ₂ Sr ₂ Ca _{n-1} Cu _n O _{2n+4+δ}	O ²⁻	[2Cu ³⁺] ²⁺	125	Planar Cu-O ₄
HgSr ₂ Ca _{n-1} Cu _n O _{2n+2+δ}	O ²⁻	[2Cu ³⁺] ²⁺	>135 [‡]	Pyramidal Cu-O ₅
(Sr _{1-x} Nd _x)CuO ₂	[Nd ³⁺] ⁺	[Cu ¹⁺] ⁻	40	Planar Cu-O ₄
(Sr _{1-x} La _x)CuO ₂	[La ³⁺] ⁺	[Cu ¹⁺] ⁻	43	Planar Cu-O ₄
(Sr _{1-x} Ca _x) _{1-y} CuO ₂	[Sr ²⁺ _{1-x} Ca ²⁺ _x] ⁻	[Cu ³⁺] ⁺	110	Planar Cu-O ₄
Sr _{1-x} CuO _{2-δ} *	[Sr ²⁺] ⁻ , [O ²⁻] ²⁺	[Cu ³⁺] ⁺ , [2Cu ¹⁺] ²⁻	—	Planar Cu-O ₄ *
Proposed				
(Ca _{1-x} Na _x)CuO ₂	[Na ¹⁺] ⁻	[Cu ³⁺] ⁺	—	Planar Cu-O ₄
(Sr _{1-x} Ag _x)CuO ₂	[Ag ¹⁺] ⁻	[Cu ³⁺] ⁺	—	Planar Cu-O ₄
(Ba _{1-x} K _x)CuO ₂ †	[K ¹⁺] ⁻	[Cu ³⁺] ⁺	—	Planar Cu-O ₄

*O²⁻ vacancies in the CuO₂ planes, indicated by the variable δ , break the continuity of the covalent transfer paths and render the material nonsuperconducting.

†This compound may not exist because of the large discrepancy between the *B* and *A* site ionic radii.

‡This compound was prepared under high pressure, which together with Hg probably increased the covalent exchange energy between the Cu ions.

TABLE 2
Ionic Radii for Cation Matching

Divalent Cation	Radius A	Monovalent Cation	Radius A
Ca ²⁺	0.99	Na ¹⁺	0.95
Sr ²⁺	1.13	Ag ¹⁺	1.26
Ba ²⁺	1.35	K ¹⁺	1.33

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REPORT DOCUMENTATION PAGE

Form Approved
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1. AGENCY USE ONLY (Leave blank)			2. REPORT DATE 10 July 1995	3. REPORT TYPE AND DATES COVERED Technical Report
4. TITLE AND SUBTITLE A Strategy for Higher Temperature Superconductivity in the Layered Cuprates			5. FUNDING NUMBERS C — F19628-95-C-0002 PR — 1	
6. AUTHOR(S) Gerald F. Dionne				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Lincoln Laboratory, MIT 244 Wood Street Lexington, MA 02173-9108			8. PERFORMING ORGANIZATION REPORT NUMBER TR-102I	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) U.S. Air Force ESC Hanscom AFB Bedford, MA 01730			10. SPONSORING/MONITORING AGENCY REPORT NUMBER ESC-TR-94-112 ESC-TR-95-015	
11. SUPPLEMENTARY NOTES None				
12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) Recent attempts to raise the critical temperatures of cuprate superconductors are reviewed and discussed in terms of covalent electron transfer between Cu ions of mixed valence. A report of possible superconductivity effects at 250 K is examined from the standpoint of ABO_2 parent-cell building blocks identified as superconducting by Goodenough and his students at the University of Texas. Based on the mounting evidence that cation mixed valence is responsible for the superconductivity in these compounds, compositions $(Ca_{1-x}Na_x)CuO_2$, $(Sr_{1-x}Ag_x)CuO_2$, and $(Ba_{1-x}K_x)CuO_2$ are proposed as chemical systems for obtaining superconductors with maximum feasible critical temperatures.				
14. SUBJECT TERMS high temperature superconductivity layered cuprate superconductors electron hopping critical temperatures			15. NUMBER OF PAGES 30	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT Same as Report	